

RECEIVED
CENTRAL FAX CENTER
JUL 14 2008

[Document Title] APPLICATION FOR PATENT
[Docket Number] P020457
[Filing Date] July 26, 2002
[To] The Commissioner of the Patent Office
[International Patent Classification] B32B 7/02
C03H 1/00
B42D 15/10
[Inventor]
[Address] c/o DAI NIPPON PRINTING CO., LTD.
1-1, Ichigaya-Kagacho 1-chome, Shinjuku-ku,
Tokyo-to, Japan
[Name] Tetsuya TONE
[Applicant]
[Identification Number] 000002897
[Name] DAI NIPPON PRINTING CO., LTD.
[Agent]
[Identification Number] 100111659
[Patent Attorney]
[Name] Satoshi KANAYAMA
[Indication of Fees]
[Prepaid Register Number] 013055
[Amount of Fee] ¥21,000
[List of Attached Documents]
[Material Name] Specification 1
[Material Name] Drawings 1
[Material Name] Abstract 1
[General Power of Attorney Number] 9808512
[Need of Proof] Need

RECEIVED
CENTRAL FAX CENTER

JUL 14 2008

[Document Title] SPECIFICATION

[Title of the Invention] VOLUME HOLOGRAM TRANSFER FOIL

[Patent Claims]

[Claim 1] A volume hologram transfer foil comprising a substrate, a volume hologram layer and a heat sensitive adhesive layer laminated sequentially, wherein the volume hologram layer has a breaking strain at 25°C in a range of 0.5% to 15%, a breaking strain at 120°C in a range of 0.5% to 30%, and the heat sensitive adhesive layer has a breaking strain at 25°C in a range of 0.5% to 15%.

[Claim 2] A volume hologram transfer foil comprising a substrate, a volume hologram layer and a heat sensitive adhesive layer laminated sequentially, wherein the volume hologram layer has a breaking strain at 25°C in a range of 0.5% to 15%, a breaking strain at 120°C in a range of 0.5% to 30%, and the heat sensitive adhesive layer has a breaking strain at 25°C in a range of 0.5% to 15%, and wherein the heat sensitive adhesive layer contains at least a synthetic resin having heat sensitive adhesiveness and an organic fine particle and/or an inorganic fine particle.

[Claim 3] The volume hologram transfer foil according to Claim 1 or 2, wherein an average particle size of the fine particle is in a range of 0.01 μm to 20 μm , and wherein a content of the fine particle is 20 parts by weight to 200 parts by weight based on 100 parts by weight of the synthetic resin having heat sensitive adhesiveness.

[Claim 4] The volume hologram transfer foil according to Claim 1 or 2, wherein the fine particle is a fluorescent fine particle.

[Claim 5] The volume hologram transfer foil according to

Claim 1 or 2, wherein the organic fine particle has thermoplasticity and has a glass transition temperature of 120°C or higher.

[Claim 6] The volume hologram transfer foil according to Claim 1 or 2, wherein the organic fine particle is a resin bead pigment.

[Claim 7] The volume hologram transfer foil according to Claim 1 or 2, wherein a delaminating layer is provided in between the substrate and the volume hologram layer.

[Claim 8] A method for manufacturing a volume hologram transfer foil to manufacture the volume hologram transfer foil of Claim 1 or 2, wherein a first film having the volume hologram layer, and a second film having the heat sensitive adhesive layer, are prepared separately in independent processes, and laminated in a subsequent process in combination, depending on the application.

[Claim 9] The method for manufacturing a volume hologram transfer foil according to Claim 7, wherein the first film having the volume hologram layer, the second film having the heat sensitive adhesive layer, and a third film having the delaminating layer are prepared separately in independent processes; a hologram image is formed on the volume hologram layer of the first film; and subsequently, the second film and the third film are laminated.

[Detailed description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a volume hologram transfer foil, and more specifically to a volume hologram transfer foil having an excellent foil cutting property which can be easily transferred to a transferred body, and to a method for manufacturing a volume hologram transfer foil.

[Prior Art]

[0002]

Conventionally, in most hologram transfer foils, surface relief type hologram having irregularity on the surface is used, and in its general structure, a substrate, a delaminating layer, surface relief type hologram layer, reflective film layer and heat sensitive adhesive layer are laminated sequentially. The surface relief type hologram layer shows an excellent foil cutting property and is used in many applications. In the case of a hologram transfer foil, since layers such as a delaminating layer, hologram layer, heat sensitive adhesive layer and the like other than the substrate are cut due to a heat mold in its heat transfer (also referred to simply as transfer, hot stamp), it is necessary that a foil cutting property is excellent and hologram is assuredly transferred to a transferred body.

[0003]

On the other hand, as materials capable of being used regarding volume hologram, silver salt materials, photopolymers and the like are mentioned, and in general, photopolymers which can be produced by a dry process are used in mass production. However, such a photopolymer is required to have low viscosity.

to increase refractive index modulation value (Δn), while also to have monomers and the like to move therefore, the hardness of a coated film itself is low. Consequently, a foil cutting property is poor and a transferring property is instable, leading to a problem that it is extremely difficult to make a transfer foil of volume hologram.

Even if the hardness of a material is increased by improving the volume hologram material itself for solving this problem, there is also a problem that it is difficult to completely improve a transferring property and refractive index cannot be modulated sufficiently by further increasing the hardness of a coated film, making the hologram darker.

Further, the one is known which the foil cutting property is improved by previously making slits on a delaminating layer, hologram layer, heat sensitive adhesive layer and the like at transferring portions and delaminating them from a slit line along a heat mold in transferring. However, this method has a problem that a slit mold for making slits and a slit process are necessary, needing time and cost.

Furthermore, the present inventors have suggested a volume hologram transfer foil having a hologram layer made of a specific material having specific breaking strain (Japanese Patent Application Laid-Open (JP-A) No. 2000-272295)). However, also in this method, since soft thermoplastic resins are often used as a heat sensitive adhesive layer in making a transfer foil, there is problems that its foil cutting property is not sufficient and its transferring property to a transferred body is not good enough.

[0004]

[Problem to be Solved by the Invention]

To solve the above-mentioned problems, the present invention is achieved. Even if the hardness of a material could be increased by improving the volume hologram material itself, it had been difficult to completely improve a transferring property while keeping the brightness of the hologram image. To solve the problems, the present invention provides a volume hologram foil having an excellent foil cutting property and having an improved transferring property enabling easy transfer to a transferred body and also a manufacturing method thereof, wherein the breaking strain of the heat sensitive adhesive layer is rendered equivalent to or lower than the breaking strain of the volume hologram layer.

[0005]

[Means for Solving the Problem]

To solve the problems, a volume hologram transfer foil recited in Claim 1 comprises a substrate, a volume hologram layer and a heat sensitive adhesive layer laminated sequentially, wherein the volume hologram layer has a breaking strain at 25°C in a range of 0.5% to 15%, a breaking strain at 120°C in a range of 0.5% to 30%, and the heat sensitive adhesive layer has a breaking strain at 25°C in a range of 0.5% to 15%. According to the present invention, by rendering the breaking strain of the heat sensitive adhesive layer equivalent to or lower than the breaking strain of the volume hologram layer, the volume hologram transfer foil is provided having an excellent foil cutting property and having an improved transferring property enabling easy transfer to a transferred body while maintaining the brightness of the hologram image.

A volume hologram transfer foil recited in Claim 2 comprises a substrate, a volume hologram layer and a heat sensitive adhesive layer laminated sequentially, wherein the volume hologram layer has a breaking strain at 25°C in a range of 0.5% to 15%, a breaking strain at 120°C in a range of 0.5% to 30%, and the heat sensitive adhesive layer has a breaking strain at 25°C in a range of 0.5% to 15%, and wherein the heat sensitive adhesive layer contains at least a synthetic resin having heat sensitive adhesiveness and an organic fine particle and/or an inorganic fine particle. According to the present invention, since the organic and/or inorganic fine particle is contained in the heat sensitive adhesive layer, fragility can be imparted thereto, and the volume hologram transfer foil can be provided having an excellent foil cutting property and having an improved transferring property enabling easy transfer to a transferred body while maintaining the brightness of the hologram image.

The volume hologram transfer foil recited in Claim 3 comprises the fine particle, wherein an average particle size thereof is in a range of 0.01 μm to 20 μm , and a content thereof is 20 parts by weight to 200 parts by weight based on 100 parts by weight of the synthetic resin having heat sensitive adhesiveness. The volume hologram transfer foil recited in Claim 4 comprises the fine particle which is a fluorescent fine particle. The volume hologram transfer foil recited in Claim 5 comprises the organic fine particle which has thermoplasticity and a glass transition temperature of 120°C or higher. The volume hologram transfer foil recited in Claim 6 comprises the organic fine particle which is a resin bead pigment. In the

present invention, a volume hologram transfer foil having an excellent foil cutting property and having an improved transferring property enabling easy transfer to a transferred body while having excellent design property background can be provided.

The volume hologram transfer foil recited in Claim 7 has a delaminating layer provided in between the substrate and the volume hologram layer. In the present invention, a volume hologram transfer foil having an excellent foil cutting property and an excellent peeling property can be provided.

The method for manufacturing a volume hologram transfer foil recited in Claim 8 is a method wherein a first film having the volume hologram layer, and a second film having the heat sensitive adhesive layer are prepared separately in independent processes, and laminated in a subsequent process in combination, depending on the application. In the present invention, lamination of the films can be conducted by a dry process, and there is no need to use a solvent. Consequently, lamination can be conducted by a simple apparatus under mild condition, and a manufacturing method advantageous for the process can be provided.

The method for manufacturing a volume hologram transfer foil recited in Claim 9 provides a method wherein the first film having the volume hologram layer, the second film having the heat sensitive adhesive layer, and a third film having the delaminating layer are prepared separately in independent processes; a hologram image is formed on the volume hologram layer of the first film; and subsequently, the second film and the third film are laminated. In the present invention, a volume

hologram transfer foil excellent in foil cutting property and peeling property can be obtained by a dry process, and there is no need to use a solvent. Consequently, lamination can be conducted by a simple apparatus under mild condition, and a manufacturing method advantageous for the process can be provided.

[0006]

[Preferred embodiment of the Invention]

Embodiments of the present invention are explained with reference to drawings.

FIG. 1 is a sectional view showing one example of the volume hologram transfer foil of the present invention.

FIG. 2 is a sectional view showing another example of the volume hologram transfer foil of the present invention.

(Layer Structure)

The volume hologram transfer foil shown in FIG. 1 presents a basic structure and has: a substrate 11, a volume hologram layer 15, a primer layer 18 if needed, and a heat sensitive adhesive layer 17 (also referred to as heat sealing layer) laminated sequentially. The volume hologram transfer foil shown in FIG. 2, is a foil with an improved transfer suitability and comprises a delaminating layer 19 in between the volume hologram layer 15 and the substrate 11.

In the volume hologram transfer foil of the present invention, as shown in FIG, 2, it is preferable to provide a delaminating layer 19 in between the volume hologram layer 15 and the substrate 11 because delaminating property between the substrate 11 and volume hologram layer 15 becomes stable at heat transfer. For enhancing close adherence between the

delaminating layer 19 and volume hologram layer 15, a primer layer may further be provided.

[0007]

In conventional volume hologram transfer foils, a flexible material has to be used as a volume hologram layer, and for obtaining a clear hologram image, it is necessary to increase the film thickness of a hologram layer, consequently, a foil cutting property is poor and a transferring property is very instable. Though it is possible to increase the hardness of a material by improving the material itself of a volume hologram layer, when the hardness of a coated film is increased too much, the brightness of a hologram image lowers and it is difficult to improve a transferring property while maintaining the brightness of a hologram image. The present applicant discloses, in JP-A No. 2000-272295, a volume hologram transfer foil in which the material of a hologram layer is limited to a material having specific breaking strain. However, since a flexible thermoplastic resin is used as a heat sensitive adhesive layer, a volume hologram transfer foil, as a whole, may not have a sufficient foil cutting property, therefore, it is desired to improve a transferring property to a transferred body.

[0008]

(Points of the invention)

The present inventors have further investigated the disclosed invention in JP-A No. 2000-272295, and resultantly found that by limiting the breaking strain of other members such as the adhesive layer and limiting the filler to be added in addition to the breaking strain of a volume hologram layer, a

foil cutting property is improved and a transferring property to a transferred body increases, leading to completion of the present invention.

Furthermore, it is necessary to select fragile materials also for other members such as a heat sensitive adhesive layer, protective layer (also called OP layer) and the like in a volume hologram transfer foil. However, regarding a heat sensitive adhesive layer which should be made of a material showing thermoplasticity at low temperature, by addition of filler, fragility can be improved and foil cutting in transferring can be helped to give excellent properties. As the measure of a foil cutting property, breaking strain which is one of mechanical strengths is used.

[0009]

(Limitation of Breaking Strain)

By limiting the breaking strain at 25°C of the volume hologram layer 15 as in a range of 0.5% to 15%, the breaking strain at 120°C as in a range of 0.5% to 30%, and the breaking strain at 25°C of the heat adhesive layer 17 as in a range of 0.5% to 15%, a foil cutting property of the volume hologram foil becomes excellent. Setting either of the volume hologram layer 15 or the heat adhesive layer 17 is insufficient in its effect.

(Limitation of Filler)

As the filler to limit the breaking strain of the heat adhesive layer 17, an organic fine particles and/or inorganic fine particles can be used.

It is preferable that an average particle size of the fine particle is in a range of 0.01 μm to 20 μm , and a content of the fine particle is 20 parts by weight to 200 parts by weight

based on 100 parts by weight of the synthetic resin having heat sensitive adhesiveness. Further, the organic fine particle preferably has thermoplasticity and a glass transition temperature of 120°C or higher. Moreover, by using the fine particle which is a fluorescent fine particle or of a resin bead pigment, a hologram transfer foil having a colored background can be provided, and further, an effect of anticounterfeit is also improved.

[0010]

(Substrate)

Next, materials constituting the substrate and other layers will be described. As examples of the substrate 11, a polyethylene terephthalate (PET) film, polyvinyl chloride (PVC) film, polyvinylidene chloride film, polyethylene film, polypropylene film, polycarbonate film, cellophane film, acetate film, nylon film, polyvinyl alcohol film, polyamide film, polyamideimide film, ethylene-vinyl alcohol copolymer film, polymethyl methacrylate (PMMA) film, polyether sulfone film, polyether ether ketone (PEEK) film and the like can be cited. The thickness of such a substrate is usually in a range of 5 μm to 200 μm , preferably in a range of 10 μm to 100 μm .

[0011]

(Material of the Volume Hologram Layer)

In general, as the material forming a volume hologram layer, known volume hologram recording materials are listed such as a silver salt material, dichromate gelatin emulsion, photo-polymerizable resin, photo-crosslinkable resin and the like, however, as the photosensitive material for forming hologram for forming the volume hologram layer 15 of the present

invention, suitably used are the following photosensitive materials (1) and (2) from the standpoint of production efficiency.

(1) Photosensitive material composed of binder resin, photo-polymerizable compound, photo-polymerization initiator and sensitizing dye.

(2) Photosensitive material composed of cationic polymerizable compound, radical polymerizable compound, photo-radical polymerization initiator system which is sensitized by light of specific wavelength to cause polymerization of radical polymerizable compound, and photo-cationic polymerization initiator system which shows low sensitivity to light of specific wavelength and which is sensitized by light of other wavelength to cause polymerization of cationic polymerizable compound.

[0012]

As the binder resin in this photosensitive material (1) are poly(meth)acrylate ester or partial hydrolyzates thereof, polyvinyl acetate or its hydrolyzate, copolymers having at least one compound selected from the group of copolymerizable monomers such as acrylic acid, acrylic ester, and the like as a polymerization component, or mixtures thereof, polyisoprene, polybutadiene, polychloroprene, polyvinyl alcohol, partial acetalized compounds of polyvinyl alcohol; namely polyvinyl acetal, polyvinyl butyral, polyvinyl acetate, vinyl chloride-vinyl acetate copolymer and the like, or mixtures thereof, and the like can be listed. Here, to stabilize recorded hologram, there is a process of heating and moving a monomer for. For this, the binder resin is preferably one having

relatively lower glass transition temperature and consequently providing easy movement of a monomer.

[0013]

As the photo-polymerizable compound, photo-polymerizable and photo-crosslinkable monomers, oligomers, prepolymers, and mixture thereof having at least one ethylenically unsaturated bond in one molecule, as described later, can be applied, and for example, unsaturated carboxylic acids and salts thereof, esters of unsaturated carboxylic acids with aliphatic polyhydric alcohol compounds, amide compounds of unsaturated carboxylic acids with aliphatic polyvalent amine compounds, and the like are listed.

[0014]

As the specific examples of monomers of unsaturated carboxylic acids, mentioned are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid and the like, and regarding the specific examples of monomers of esters of aliphatic polyhydric alcohol compounds with unsaturated carboxylic acids, as the acrylic ester, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, trimethylolpropane triacrylate, trimethylolpropane tri(acryloyloxypropyl) ether, trimethylolethane triacrylate and the like are listed.

[0015]

As the methacrylate ester, tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolpropane trimethacrylate,

trimethylolethane trimethacrylate and the like are listed. As the itaconate ester, ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butane diol diitaconate and the like are listed. As the crotonate ester, ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, sorbitol tetracrotonate and the like are listed. As isocrotonate ester, ethylene glycol diisocrotonate, pentaerythritol diisocrotonate, sorbitol tetraisocrotonate and the like are listed. As the maleate ester, ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate, sorbitol tetramaleate and the like are listed.

[0016]

As the halogenated unsaturated carboxylic acid, 2,2,3,3-tetrafluoropropyl acrylate, 1H,1H,2H,2H-heptafluorodecyl acrylate, 2,2,3,3-tetrafluoropropyl methacrylate and the like are listed. As the specific examples of monomers of amides of unsaturated carboxylic acids with aliphatic polyvalent amine compounds, methylenebisacrylamide, methylenebismethacrylamide, 1,6-hexamethylenebisacrylamide, 1,6-hexamethylenebismethacrylamide and the like are listed.

[0017]

As the photo-polymerization initiator in the initiator system, 1,3-di(t-butylldioxycarbonyl)benzophenone, 3,3',4,4'-tetrakis(t-butylldioxycarbonyl)benzophenone, N-phenylglycine, 2,4,6-tris(trichloromethyl)-s-triazine, 3-phenyl-5-isooxazolone, 2-mercaptobenzimidazole, imidazole dimers and the like are exemplified. It is preferable that the photo-polymerization initiator is subjected to a decomposition

treatment after recording hologram from the standpoint of stabilization of the recorded hologram. For example, the organic peroxide system is preferable since it is easily decomposed by irradiation with ultraviolet ray.

[0018]

As the sensitizing dye, thiopyrylium salt-based dyes, merocyanine-based dyes, quinoline-based dyes, styrylquinoline-based dyes, ketocoumarin-based dyes, thioxanthene-based dyes, xanthene-based dyes, oxonol-based dyes, cyanine dyes, rhodamine dyes, thiopyrylium salt-based dyes, pyrylium ion-based dyes, diphenyl iodonium ion-based dyes and the like showing light absorption at 350 to 600 nm are exemplified. It may also be a sensitizing dye showing light absorption in the wavelength range of 350 nm or less or 600 nm or more.

[0019]

The compounding ratio of a photosensitive material composed of the binder resin, the photo-polymerizable compound, the photo-polymerization initiator and the sensitizing dye is as described below. The photo-polymerizable compound is used in a proportion of 10 parts by weight to 1000 parts by weight, preferably of 10 parts by weight to 100 parts by weight based on 100 parts by weight of the binder resin. The photo-polymerization initiator is used in a proportion of 1 part by weight to 10 parts by weight, preferably of 5 parts by weight to 10 parts by weight based on 100 parts by weight of the binder resin. The sensitizing dye is used in a proportion of 0.01 part by weight to 1 part by weight, preferably of 0.01 part by weight to 0.5 parts by weight based on 100 parts by weight of the binder

resin. Additionally, as the components of a material for forming volume hologram, for example, plasticizers, glycerin, diethylene glycol, triethylene glycol and various nonionic surfactants, cationic surfactants, anionic surfactants and the like are listed.

[0020]

The photosensitive materials (1) are made into coating solution having a solid content of 15% to 25% using methyl ethyl ketone, cyclohexanone, xylene, tetrahydrofuran, ethylcellosolve, methylcellosolve acetate, ethyl acetate, isopropanol and the like by itself or as a mixed solvent thereof. The volume hologram layer is formed by using the coating solution and coating it by bar coat, spin coat or dipping and the like when a supporting body is in the form of sheet (each one sheet). When a supporting body is in the form of long roll, coating is conducted by gravure coat, roll coat, die coat or comma coat and the like, and drying is conducted and/or if necessary hardening is conducted. The thickness of thus obtained volume hologram-forming material is from 0.1 μm to 50 μm , preferably from 5 μm to 20 μm , and if necessary, a protective film may be laminated. As the protective film, a resin film having high transparency and having high smoothness such as a polyethylene terephthalate film, polypropylene film, polyvinyl chloride film and the like having a thickness of 10 μm to 100 μm may advantageously be pasted by rubber rollers and the like. Further, as the photosensitive material, OMNIDEX 801, commercial product manufactured by Du Pont Kabushiki Kaisha, and the like may be used, for example.

[0021]

On the photosensitive material (1), recording is conducted by using laser light of two light fluxes. As this laser light, for example, light having a wavelength of 633 nm by helium-neon ion laser, light having a wavelength of 514.5 nm, 488 nm, 457.9 nm by argon ion laser, and light having a wavelength of 647.1 nm, 568.2 nm, 520.8 nm by krypton ion laser, in the visible light quantity range, further, light having a wavelength of 337.5 nm, 350.7 nm, 356.4 nm by krypton ion laser (1.5 W), and light having a wavelength of 351.1 nm, 368.8 nm by argon ion laser (40 mW), light having a wavelength of 332.4 nm by neon ion laser (50 mW), light having a wavelength of 325.0 nm by cadmium ion laser (15 mW) and the like can be applied. [0022]

Of them, one wavelength is taken out, and interference fringe is recorded using a wavelength rendering a photo-polymerization initiator to be excited, interference light of object light and reference light is recorded, or a protective film is peeled off, then, an original plate of volume hologram is closely adhered to a volume hologram-forming material, laser is directed from the side of the supporting body of the volume hologram-forming material, and interference fringe of reflective light from the original plate and incident light is recorded, to give information of volume hologram. By this, single color hologram or color hologram can be obtained. Thereafter, stable volume hologram is obtained through a process of decomposing a photo-polymerization initiator by irradiation with ultraviolet ray of 0.1 to 10000 mJ/cm², preferably of 10 to 1000 mJ/cm² from a light source such as an extra-high pressure mercury lamp, high pressure mercury lamp, carbon arc, xenon arc,

metal halide lamp and the like, and a heat treatment process in which a photo-polymerizable compound is diffused and moved, for example, by heating at 120°C for 120 minutes, or other processes.

[0023]

The photosensitive material (2) is composed of a cationic polymerizable compound which is in liquid form at room temperature, a radical polymerizable compound, a photo-radical polymerization initiator system which is sensitized by light of specific wavelength to cause polymerization of the radical polymerizable compound, and a photo-cationic polymerization initiator system which shows low sensitivity to light of the above mentioned specific wavelength and which is sensitized by light of other wavelength to cause polymerization of the cationic polymerizable compound.

[0024]

This photosensitive material is coated on a supporting body, then, irradiated with light such as laser light or the like which sensitizes the photo-radical polymerization initiator system, then, irradiated with light of other wavelength than that of the above mentioned laser light which sensitizes the photo-cationic polymerization initiator system, to cause recording of hologram. First, the radical polymerizable compound is polymerized by irradiation with light such as laser light or the like (hereinafter, referred to as first exposure). Then, after polymerizing the compounds in the composition, the cationic polymerizable compound is cationic-polymerized by a Broensted acid or Lewis acid generated by decomposition of the photo-cationic polymerization initiator

system, by whole surface exposure conducted subsequently (hereinafter, referred to as post exposure).

[0025]

As the cationic polymerizable compound, which is in liquid form at room temperature is used since polymerization of a radical polymerizable compound is preferably conducted in a composition of relatively low viscosity. As such a cationic polymerizable compound, diglycerol diether, pentaerythritol polydiglycidyl ether, 1,4-bis(2,3-epoxypropoxy fluoroisopropyl) cyclohexanone, sorbitol polyglycidyl ether, 1,6-hexanediol glycidyl ether, polyethylene glycol diglycidyl ether, phenyl glycidyl ether and the like are listed.

[0026]

As the radical polymerizable compound, that having at least one ethylenically unsaturated double bond in the molecule is preferable. It is preferable that the average refractive index of a radical polymerizable compound is larger than the average refractive index of the cationic polymerizable compound, and particularly larger by 0.02 or more. When difference in the average refractive index is not more than the above mentioned value, modulation of refractive index becomes insufficient and not preferable. As the radical polymerizable compound, for example, acrylamide, methacrylamide, styrene, 2-bromostyrene, phenyl acrylate, 2-phenoxyethyl acrylate, 2,3-naphthalene dicarboxylic acid (acryloxyethyl) monoester, methylphenoxyethyl acrylate, nonylphenoxyethyl acrylate, β -acryloxyethyl hydrogen phthalate and the like are listed.

[0027]

The photo-radical polymerization initiator system may be

an initiator system which, by first exposure for production of hologram, generates an active radical, and the active radical polymerizes a radical polymerizable compound, alternatively, a sensitizer which is in general a component absorbing light may be used in combination with an active radical-generating compound or acid-generating compound. As the sensitizer in such a photo-radical polymerization initiator system, color compounds such as dyes are often used for absorbing visible laser light, however, in the case of colorless transparent hologram, use of a cyanine-based dye is preferable. The reason for this is that, since a cyanine-based dye is in general easily decomposed by light, when it is left for from several hours to several days under room light or solar light, or by post exposure in the present invention, a dye in hologram is decomposed to lose absorption in the visible range, and colorless transparent volume hologram can be obtained.

[0028]

The specific examples of the cyanine-based dye include anhydro-3,3'-dicarboxymethyl-9-ethyl-2,2'-thiacarbocyanine betaine, anhydro-3-carboxymethyl-3',9'-diethyl-2,2'-thiacarbocyanine betaine, 3,3',9-triethyl-2,2'-thiacarbocyanine iodine salt, 3,9-diethyl-3'-carboxymethyl-2,2'-thiacarbocyanine iodine salt, 3,3',9-triethyl-2,2'-(4,5,4',5'-dibenzo)thiacarbocyanine iodine salt, 2-[3-(3-ethyl-2-benzothiazolidene)-1-propenyl]-6-[2-(3-ethyl-2-benzothiazolidene)ethylideneimino]-3-ethyl-1,3,5-thiadiazolium iodine salt, 2-[[3-allyl-4-oxo-5-(3-n-propyl-5,6-dimethyl-2-benzothiazolidene)-ethylidene-2-thiazolinylidene]methyl]3-ethyl-4,5-diphenylthiazolinium iodine salt,

1,1',3,3',3',3'-hexamethyl-2,2'-indotricarbocyanine iodine salt, 3,3'-diethyl-2,2'-thiatricarbocyanine perchlorate, anhydro-1-ethyl-4-methoxy-3'-carboxymethyl-5'-chloro-2,2'-quinothiacyanine betaine, anhydro-5,5'-diphenyl-9-ethyl-3,3'-disulfopropylloxycarbocyanine hydroxide triethylamine salt and the like, and these can be used by itself or in combination of two or more kinds.

[0029]

As the active radical-generating compound which may be used in combination with a cyanine-based dye, diaryl iodonium salts, or 2,4,6-substituted-1,3,5-triazines are listed. When high photo-sensitivity is necessary, use of diaryl iodonium salts is particularly preferable. As the specific examples of the diaryl iodonium salts, chlorides, bromides, tetrafluoroborates, hexafluorophosphates, hexafluoroarsenates, hexafluoroantimonates, trifluoromethanesulfonates, 9,10-dimethoxyanthracene-2-sulfonates and the like of diphenyl iodonium, 4,4'-dichlorodiphenyl iodonium, 4,4'-dimethoxydiphenyl iodonium, 4,4'-ditertiarybutyldiphenyl iodonium, 3,3'-dinitrodiphenyl iodonium and the like are listed. Specific examples of 2,4,6-substituted-1,3,5-triazines include 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine, 2,4,6-tris(trichloromethyl)-1,3,5-triazine, 2-phenyl-4,6-bis(trichloromethyl)-1,3,5-triazine, 2,4-bis(trichloromethyl)-6-(p-methoxyphenylvinyl)-1,3,5-triazine, 2-(4'-methoxy-1'-naphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine and the like.

[0030]

The photo-cationic polymerization initiator system may advantageously be an initiator system which shows low sensitivity to the first exposure and which is sensitized by the post exposure irradiated with light of different wavelength from the wavelength of the first exposure to generate a Broensted acid or Lewis acid, and to cause polymerization of the cationic polymerizable compound, and that which does not cause polymerization of a cationic polymerizable compound during the first exposure is particularly preferable. As the photo-cationic polymerization initiator system, for example, diaryl iodonium salts, triaryl sulfonium salts, iron allene complexes and the like are listed. As the preferable diaryl iodonium salts, tetrafluoroborates, hexafluorophosphates, hexafluoroarsenates, hexafluoroantimonates and the like of iodonium shown for the above mentioned photo-radical polymerization initiator system are listed. As the preferable triaryl sulfonium salts, triphenyl sulfonium, 4-tertiary-butyltriphenylsulfonium and the like are listed.

[0031]

If necessary, in the composition of the photosensitive material, the photosensitive material may be used together with a binder resin, heat polymerization preventing agent, silane coupling agent, plasticizer, coloring agent and the like. The binder resin is used when the film forming property of a composition before hologram formation or evenness of film thickness is improved, or used for stable presence of interference fringe formed by polymerization by irradiation with light such as laser light and the like, until post exposure. The binder resin may advantageously be one showing excellent

solubility with a cationic polymerizable compound and radical polymerizable compound, and for example, chlorinated polyethylene, polymethyl methacrylate, copolymer of methyl methacrylate and other alkyl ester (meth)acrylate, copolymer of vinyl chloride and acrylonitrile, polyvinyl acetate and the like are listed. The binder resin may have reactivity of a cationic polymerizable group and the like at its side chain or main chain.

[0032]

In the composition of a photosensitive material, the proportion of the cationic polymerizable compound is 2 wt% to 70 wt%, preferably 10 wt% to 50 wt%, the proportion of the radical polymerizable compound is 30 wt% to 90 wt%, preferably 40 wt% to 70 wt%, the proportion of the photo radical polymerization initiator is 0.3 wt% to 8 wt%, preferably 1 wt% to 5 wt%, the proportion of the photo cationic polymerization initiator system is 0.3 wt% to 8 wt%, preferably 1 wt% to 5 wt%, based on the total weight of the composition. The above-mentioned composition of photosensitive material can be prepared by mixing essential components and optional components as they are in cold and dark place using for example a high speed stirring machine, or if necessary, by compounding with for example a ketone-based solvent such as methyl ethyl ketone and the like, an ester-based solvent such as ethyl acetate and the like, an aromatic solvent such as toluene and the like, a cellosolve-based solvent such as methylcellosolve and the like, an alcohol-based solvent such as methanol and the like, an ether-based solvent such as tetrahydrofuran, dioxane and the like, or a halogen-based solvent such as dichloromethane, chloroform and the like.

[0033]

A recording layer composed of such photosensitive materials can be formed by coating the composition of the photosensitive materials by the same coating method as for the photosensitive material (1) and drying the coated film. The coating amount is appropriately selected, and the film thickness after drying can be, for example, from 1 μm to 50 μm .

[0034]

In the recording layer composed of such photosensitive materials (2), interference fringe is recorded inside with a general holography exposing apparatus by polymerizing a radical polymerizable compound using, for example, laser light having a wavelength from 300 to 1200 nm. At this stage, diffracted light is obtained by the recorded interference fringe, and hologram is formed, however, for further polymerization of a cationic polymerizable compound remaining un-reacted, it is preferable to form hologram by whole surface irradiation with light having a wavelength of 200 nm to 700 nm at which a photo-cationic polymerization initiator system is sensitized, as post exposure. It is also possible to change diffraction efficiency, peak wavelength of diffracted light, half bandwidth and the like by treating a layer for forming volume hologram with heat or infrared ray before post exposure.

[0035]

For the hologram forming layer formed by the above-mentioned hologram forming materials to have excellent foil cutting property at the time of transfer, the cured volume hologram layer needs to have a breaking strain at 25°C in a range of 0.5% to 15%, a breaking strain at 120°C in a range of 0.5%

to 30%. If the braking strain is out of the above ranges, the cutting of the foil becomes insufficient and transfer of the hologram becomes difficult. Preferable breaking strain is 1% to 10% and 1% to 20%, respectively.

[0036]

Further, the volume hologram layer 15 of the present invention preferably has a glass transition temperature of about 80°C. Therefore, for setting the breaking strain within the above mentioned range, it is necessary to previously determine the curing conditions of the selected hologram forming materials by previous experiments.

[0037]

(Heat Adhesive Layer)

The heat adhesive layer (heat sealing layer) 17 comprises at least a synthetic resin having heat sensitive adhesiveness and a filler. As the examples of the synthetic resin having heat sensitive adhesiveness, an ethylene-vinyl acetate copolymer resin, vinyl chloride-vinyl acetate copolymer resin, polyamide resin, polyester resin, polyethylene resin, ethylene-isobutyl acrylate copolymer resin, polybutyral resin, polyvinyl acetate and its copolymer resin, ionomer resin, acid-denaturated polyolefin-based resin, (meth)acrylic resin such as acrylic resin and methacrylic resin, acrylic acid ester-based resin, ethylene-(meth)acrylic acid copolymer, ethylene-(meth)acrylate ester copolymer, polymethyl methacrylate-based resin, cellulose-based resin, polyvinyl ether-based resin, polyurethane resin, polycarbonate resin, polypropylene resin, epoxy resin, phenol resin, vinyl-based resin, maleic acid resin, alkyd resin, polyethylene oxide resin,

urea resin, melamine resin, melamine-alkyd resin, silicone resin, rubber-based resin, thermoplastic resins such as SBS, SIS, SEBS, SEPS can be cited. These resins can be used alone or in combination. Preferable is a composition composed of an ethylene-vinyl acetate copolymer resin (EVA) and having a vinyl acetate content of 25% or more and capable of being heat-sealed at temperatures of 180°C or lower. Furthermore, additives such as a dispersing agent, filler, plasticizer, antistatic agent and the like may be appropriately added, if necessary. As the antistatic agent, nonionic surfactants, anionic surfactants, cationic surfactants and the like, and polyamides and acrylic acid derivatives and the like can be applied. The heat sensitive adhesive layer may also be colored.

[0038]

(Filler)

As the filler, there are listed organic fine particles and/or inorganic fine particles. As the inorganic fine particles, for example, calcium carbonate, calcium silicate, clay, kaolin, talc, silica, glass, diatomaceous earth, mica powder, alumina, magnesium oxide, zinc oxide, barium sulfate, aluminum sulfate, calcium sulfate, basic magnesium carbonate, molybdenum disulfide and the like can be applied. The organic fine particles are preferably a thermoplastic resin having a glass transition temperature of 120°C or more, and fine particles of, for example, WAX, polyethylene, fluorine-based resin, acrylic resin, methacrylic resin, phenol resin, urea resin, melamine resin, epoxy resin, unsaturated polyester resin and the like (thermosetting resins), copolymers of polystyrene, styrene and/or α -methylstyrene with other monomers (for example,

maleic anhydride, phenylmaleimide, methyl methacrylate, butadiene, acrylonitrile and the like) (for example, AS resin, ABS resin, MBS resin, heat resistant ABS resin and the like) and the like can be applied.

[0039]

The average particle size of the filler is about 0.001 μm to 30 μm , preferably about 0.01 μm to 20 μm . The reason for this is that when the average particle size of the filler is smaller than the range, the foil cutting property is poor and when larger than the range, dispersibility is poor, the smoothness is lost, and there is a possibility of exerting an adverse influence on a hologram image. The content of filler is about 10 parts by weight to 500 parts by weight, preferably about 20 parts by weight to 200 parts by weight based on 100 parts by weight of a synthetic resin constituting a heat sensitive adhesive layer. The reason for this is that when the content of the filler is smaller than the range, a foil cutting property is poor, and when larger than the range, dispersibility is poor, unevenness occurs in fragility, and the foil cutting property becomes instable. Further reason for this is that there is also a possibility of occurrence of decrease in adhesion with an adhered body. The shape of fine particles is not particularly limited, and it may be in a form of, for example, sphere, rectangular parallelepiped, plate, scale, needle, hollow body and the like.

[0040]

When organic fine particles are used as the filler, refractive index with a binder (synthetic resin) having heat sensitive adhesiveness constituting a heat sensitive adhesive

layer 17 to be mentioned later is relatively close, therefore, a heat sensitive adhesive layer can get transparency. Coloration can be conducted also by using a material containing an inorganic pigment incorporated. Further, the fragility of a heat sensitive adhesive layer can be improved easily by controlling a functional group on the surface of a particle in comparison with inorganic particles. By using of such fluorescent fine particles or resin bead pigment as the filler, hologram having a colored background can be obtained in transferring volume hologram, further, in the case of addition of fluorescent fine particles, an effect of anticounterfeit is also improved.

[0041]

(Fluorescent Fine Particle)

As fluorescent fine particles, for example, ultrafine particles obtained by using an in-gas vaporization method from a mixture of zinc oxide (ZnO), silicon oxide (SiO₂) and manganese dioxide (MnO₂), fine particle metals obtained by applying and calcinating an organic metal compound containing a metal emitting fluorescence (Zn, Mg, Cd, Gd, Y, In, Si, Al, lanthanoid series and the like) to decompose and remove an organic component, and the like can be applied.

Specifically, a fluorescent fine particle dispersion prepared by dispersing fluorescent fine particles in a solvent is used. For example, Lumicol NKW 2102 (green), 2103 (red), 2108 (blue) and the like manufactured by Nippon Keiko K.K. are listed. SW-12 (green), SW-13 (red), SW-18 (blue) and the like manufactured by SINLOIHI CO., LTD are also listed. When such fluorescent fine particles are used, a heat sensitive adhesive

layer emits fluorescence to give a hologram image having a specific background when irradiated with ultraviolet ray, and fabrication can be judged by the presence or absence of its emission, therefore, an effect of anticounterfeit can be improved.

[0042]

(Resin Bead Pigment)

The resin bead pigment can be obtained by dispersing a fine powder of a pigment in a synthetic resin and molding the resin into particles. As the material of the bead pigment, there are listed, for example, those obtained by coating the surface of a fine powder of a pigment such as Fe_2O_3 , TiO_2 , CaCO_3 , quinacridone pigment and the like with a resin having elasticity such as polyurethane, acryl, epoxy, polyester, nylon, fluorine resin, vinyl chloride resin and the like or adding a plasticizer, stabilizer, surfactant and the like to such a resin as necessity, or those obtained by dispersing such a pigment powder in the elastic resin. The color of the bead pigment may be optionally selected depending on the desire, and for example, pearl tone using a colorless transparent bead pigment, multi-color combining bead pigments of two or more colors, and the like are also possible.

[0043]

The heat sensitive adhesive layer 17 is formed by dispersing or dissolving a synthetic resin having the heat sensitive adhesive property and the fine particles into a solvent, applying the dispersion or solution by a coating method such as roll coat, reverse roll coat, gravure coat, gravure reverse coat, comma coat, bar coat, wire bar coat, rod coat,

kiss coat, knife coat, die coat, flow coat, dip coat, spray coat and the like, and drying and/or curing the coated film. The thickness of the heat sensitive adhesive layer 17 is usually from about 0.5 μm to 20 μm , preferably from about 1 μm to 10 μm . The reason for this is that, with the thickness of less than the range, adhesion with a transferred body is not sufficient, and with the thickness over this range, a foil cutting property is poor and heating temperature in transferring has to be enhanced.

[0044]

To obtain excellent foil cutting property which allows easy cutting at the time of transfer, the breaking strain of the heat sensitive adhesive layer 17 at 25°C needs to be in a range of 0.5% to 15%. When the breaking strain is out of this range, the foil cutting property is poor and transfer of the hologram becomes difficult. Preferable breaking strain is in a range of 1% to 10%. As one of the methods to obtain a preferable breaking strain, there is a method of adjusting the breaking strain by adding the filler to the synthetic resin having heat sensitive adhesiveness. The content of the filler in the method is 20 parts by weight to 500 parts by weight, preferably 20 parts by weight to 200 parts by weight, based on 100 parts by weight of the synthetic resin having heat sensitive adhesiveness.

[0045]

(Delaminating Layer)

As the delaminating layer 19, there can be used for example acrylic and methacrylic resins such as polymethyl acrylate, polymethyl methacrylate, and polyvinyl chloride resin, cellulose resin, silicone resin, chlorinated rubber, casein,

various surfactants, metal oxides and the like by itself or in a mixture of two or more kinds. Particularly, the delaminating layer is preferably formed by appropriately selecting materials so that the delaminating force between the substrate and the transfer layer is 1 to 5 g/2.54 mm width (90° delamination). The delaminating layer 19 can be formed on the surface of the substrate by making the resin and the like into ink and using a known method such as coating method and the like, and its thickness is preferably in a range of 0.1 μm to 2 μm in view of delaminating force, foil cutting and the like. This delaminating layer 19 can also perform a function as a protective layer when a transferred body is distributed or used, since it is exposed to the outermost surface after transferred to a transferred body. In such a case, it is also called delaminating protective layer in some cases.

[0046]

(Delaminating Paper)

The delaminating papers 101H, 102H and 1012HH have delaminating properties at one surface of each substrate film, referred to as so-called "sepa" paper (also called separating paper, delaminating paper) by those skilled in the art, such as high quality paper, coat paper, impregnated paper, plastic film and the like. As the substrate film of the delaminating paper used in the present invention, polyethylene terephthalate is suitable from the standpoint of surface smoothness, heat resistance and the like, and this is also called a surface delaminating treated type PET film. The thickness of the plastic film is not particularly limited and usually from about 6 μm to 250 μm , suitably from 12 μm to 100 μm . The reason for

this is that when less than this range, mechanical strength lacks so that cutting and wrinkle are generated, due to small thickness, and over this range, strength is excess and cost is high.
(Releasing Layer)

The releasing layer used in the delaminating paper is not particularly limited as long as it is made of a material showing delaminating property, and for example, silicone resins, organic resin denatured silicone resins, fluorine resins, aminoalkyd resins, polyester resins and the like are listed. As these resins, any of emulsion type, solvent type and non-solvent type can be used.

(Thickness of Releasing Layer)

The thickness of the releasing layer is not particularly limited and usually can be from about 0.01 μm to 3 μm , preferably from about 0.05 μm to 1 μm . The reason for this is that when this thickness is less than 0.01 μm , coating of a substrate film is not sufficient and poor delamination generates, on the other hand, when the thickness is larger than 3 μm , the absolute amount of unreacted materials and silicone of lower molecular weight increases, causing migration of silicone of lower molecular weight and blocking. It is preferable that the delaminating force of the releasing layer is from about 1 to 2000 mN/cm, further from 100 to 1000 mN/cm to an adhesive tape. When the delaminating force of the releasing layer is less than 1 mN/cm, delaminating force from an adhesive sheet and non-adhesive agent is weak, and delamination and partial lifting occur. When over 2000 mN/cm, the delaminating force of a releasing layer is strong, making it difficult to delaminate. Preferable are curing type silicone resins for delaminating paper of adding type and/or

polycondensation type mainly composed of polydimethylsiloxane from the standpoint of stable delaminating property and processability.

[0048]

(Formation of Releasing Layer for Delaminating Paper)

For obtaining the releasing layer, coating solution prepared by dispersing and/or dissolving releasing layer components is coated on one surface of the substrate film, and dried with heating and/or cured. As the method of coating the coating solution, any known coating method can be used, and for example, roll coat, reverse roll coat, gravure coat, gravure reverse coat, comma coat, bar coat, wire bar coat, rod coat, kiss coat, knife coat, die coat, flow coat, dip coat, spray coat and the like are listed. The releasing layer may be formed on at least one surface or on some parts of the both surfaces of a substrate film, as needed.

[0049]

FIG. 3 is an explanatory view showing an example of transfer of the volume hologram transfer foil of the present invention.

(Transfer)

In conducting transfer using the volume hologram transfer foil of the present invention, the volume hologram transfer foil of the present invention is laminated on the surface of a transferred body to be endowed with hologram so that the heat sensitive adhesive layer 17 of the transfer foil contacts the surface, and heating and pressing with a stamper (transfer type) is conducted from the side of the substrate of the transfer foil at parts to be endowed with hologram to melt and adhere the heat

sensitive adhesive layer at the desired parts, as shown for example in FIG. 3. Then, by delaminating the transfer foil, the volume hologram layer 15 and heat sensitive adhesive layer 17 will be broken and only a transfer layer at desired parts is transferred, hologram can be imparted to the surface of a transferred material. In this operation, it is important that the volume hologram layer 15 and heat sensitive adhesive layer 17 can be broken easily, and in the present invention, tendency of breaking is represented by breaking strain.

[0050]

(Delaminating Layer)

Further, in the present invention, a barrier layer (not shown in the drawings) may also be formed either between the delaminating layer 19 and volume hologram layer 15, or between the volume hologram layer 15 and heat sensitive adhesive layer 17, or in both positions. Depending on combination of photosensitive materials, delaminating layer and heat sensitive adhesive layer (heat sealing layer) used in the method for manufacturing recited in the present invention, migration of a component of lower molecular weight from a volume hologram layer 15 to another layer occurs by time, and when, owing to this, the peak wavelength of the recorded hologram shifts to the blue side (shorted wavelength side) or this shifts to a delaminating layer and the like, its delaminating property may change in some cases. By providing such a barrier layer, these disturbance factors can be solved.

[0051]

For enhancing adhesion between a volume hologram layer 15 and heat sensitive adhesive layer 17, a primer layer 16 may

also be formed, if necessary. As such a primer layer, there can be used, for example, polyurethane, polyester, polyvinyl chloride-based resin, polyvinyl acetate-based resin, vinyl chloride-vinyl acetate copolymer, acrylic resin, polyvinyl alcohol-based resin, polyvinyl acetal resin, copolymer of ethylene with vinyl acetate or acrylic acid and the like, epoxy resin and the like.

[0052]

A primer layer 16 may also be formed by dissolving or dispersing the resin appropriately in a solvent to give coating solution, and coating by a known coating method and drying this. The coating solution may also be formed by combining the resin with a monomer, oligomer, prepolymer and the like and a reaction initiator, curing agent, cross-linking agent and the like, or by combining a main agent with a curing agent and then coating, drying and, if necessary, reacting them by conducting aging treatment. The thickness of such a primer layer is from about 0.05 to 10 μm , preferably from about 0.1 to 5 μm .

[0053]

(Barrier Layer)

The material used in such a barrier layer is not particularly limited as long as it is a material manifesting its barrier property, and usually, its object can be attained by using a transparent organic resin material. It is preferable to use a non-solvent type 3 or more functional, preferably 6 or more functional ionizing radiation-curing epoxy denatured acrylate resin, urethane denatured acrylate resin, acryl denatured polyester resin and the like reacting to ionizing radiation such a ultraviolet ray, electron beam and the like,

and particularly, urethane denatured acrylate resins are further preferable because of its high barrier property.

[0054]

The ionizing radiation-curing resin having a molecular weight in a range of 500 to 2000 is preferable in view of its coating suitability, hardness of a barrier layer finally obtained, and the like. Since the coating of the barrier layer basically contains non solvent, it can be laminated on any of a volume hologram layer 15, delaminating layer 19 and heat sensitive adhesive layer 17.

[0055]

(Manufacturing Method)

Next, a method for manufacturing the volume hologram transfer foil will be described. The preferable method for manufacturing a volume hologram transfer foil of the present invention is a method in which the first film having a volume hologram layer 15, the second film having a heat sensitive adhesive layer 17, and the third film having delaminating layer 19 are prepared separately in independent processes, and they are laminated in the subsequent process in combination, depending on the application.

[0056]

Specifically, first, the first film having a volume hologram layer 15, the second film having a heat sensitive adhesive layer 17, and the third film having delaminating layer 19 are prepared separately in independent processes. Subsequently, a hologram image is formed on a volume hologram layer 15 of the first film, then, the second film and if necessary the third film are laminated. Here, lamination of the first

or third film can be conducted by a dry process, and there is no need to use a solvent, consequently, lamination can be conducted by a simple apparatus under mild condition, being advantageous for the process.

[0057]

Further, the present invention also includes a method in which a film having a volume hologram layer 15 and delaminating layer 19 and a film having a heat sensitive adhesive layer 17 are prepared respectively by independent processes, a method in which a film having a volume hologram layer 15 and a heat sensitive adhesive layer 17 and a film having a delaminating layer 19 are prepared respectively by independent processes. Furthermore, the present invention also includes a method in which a volume hologram image is recorded on the volume hologram layer 15 of the first film, then, the third film is laminated, a development treatment is conducted, and the second film is laminated on this.

[0058]

The sectional views of the first film, second film and third film used in manufacturing of a volume hologram transfer foil of the present invention are shown in FIGS. 4A, 4B and 4C. In FIGS. 4A, 4B and 4C, for easy understanding of the layer constitution, from the upper position, FIG. 4A shows a third film, FIG. 4B shows a first film and FIG. 4C shows a second film. When a substrate body or delaminating paper is present between films, they are delaminated, and the exposed layers are laminated. As the laminating method, it may be laminated, in general, by a simple dry process method in which layers are passed through between two rolls heated or not heated, or layers

are sandwiched between plates heated or not heated and pressed.
[0059]

The first film shown in FIG. 4B is produced by forming a volume hologram layer 15 on a substrate 101K made of polyethylene terephthalate (abbreviated as PET), further laminating a delaminating layer PET as delaminating paper 101H (substrate 101K/volume hologram layer 15/delaminating paper 101H). In this case, the cohesion force of the volume hologram layer is weak, therefore, a substrate 101K may be used instead of the delaminating paper 101H to give a first film (substrate 101K/volume hologram layer 15/substrate 101K). In recording a volume hologram layer, as PET on the side irradiated with laser light, optical PET showing small drawing alignment and having small double refraction is optimal.

The second film shown in FIG. 4C is produced by forming a heat sensitive adhesive layer 17 on delaminative PET as delaminating paper 102HH, and forming delaminative PET as delaminating paper 102H on the heat sensitive adhesive layer 17 (delaminating paper 102HH/heat sensitive adhesive layer 17/delaminating paper 102H). In this case, since the heat sensitive adhesive layer 17 has no adhering property at normal temperature, either of the delaminating paper may not be present.

Further, the third film illustrated in FIG. 4A is that produced by forming a delaminating layer 19 on a substrate 103K made of PET and the like (substrate 103K/ delaminating layer 19).

[0060]

A volume hologram transfer foil can be formed by using

the first to third films described above. First, a predetermined hologram image is recorded (exposed) on the volume hologram layer 15 of the first film, then, the delaminating layer 101H is delaminated and removed, and the delaminating layer 19 of the third film and the volume hologram layer of the first film are laminated under heating (for example, 100°C to 180°C) so that they face to each other.

Next, this is introduced into a development treatment line, a predetermined heating treatment and UV treatment are performed, to fix the recorded image. Further, the delaminating paper 101K laminated on the volume hologram layer 15 is delaminated and removed to exposed the volume hologram layer 15, and the heat sensitive adhesive layer 17 of the second film and the volume hologram layer 15 are laminated under heating (for example, 100°C to 180°C) so that they face to each other, to give a layer constitution of substrate 103K/delaminating layer 19/volume hologram layer 15/heat sensitive adhesive layer 17/delaminating paper 102H. By delaminating the delaminating paper 102H from such a structure, a transfer foil shown in FIG. 2 can be obtained. Depending on application, a layer constitution of substrate 101K/volume hologram layer 15/heat sensitive adhesive layer 17/delaminating paper 102H may also be provided without using the third film.

[0061]

The method of transferring the volume hologram transfer foil to a transferred body is as described above. The article as transferred body, is not particularly limited, and for example, it can be applied to plastic cards, portable telephones, premium tickets, daily necessities or, body of CD-ROM or

wrapping or packages, and the like.

[0062]

Here, the present invention also includes a method of controlling interlayer adhesion force of each films of the first or the third films. Namely, it is preferable that, in the layer structure of a transfer foil, the relative correlation of interlayer adhesion force A between the delaminating layer 19 and substrate 103K, interlayer adhesion force B between the delaminating layer 19 and volume hologram layer 15 and interlayer adhesion force C between the volume hologram layer 15 and heat sensitive adhesive layer 17 and the value of this B satisfy the following correlation.

[0063]

Interlayer adhesion force: $C, B > A$

B value: 600 gf/2.54 mm width

In a preferable embodiment of the present invention, it is particularly preferable that the delaminating layer comprises an acrylic resin having a molecular weight of about 20000 to 100000 by itself, or such an acrylic resin and a vinyl chloride-vinyl acetate copolymer resin having a molecular weight of 8000 to 20000, further containing 1 to 5 wt% of a polyester resin having a molecular weight of 1000 to 5000 as an additive.

[0064]

The second film can have a constitution comprising delaminating paper 102HH, adhesive layer 17 and delaminating paper 102H in which both surfaces are composed of a delaminating layer. As described above, in delaminating one delaminating paper from the second film, if delaminating forces of

delaminating paper on both sides are the same, delamination of only one of the delaminating paper cannot be done smoothly. Therefore, a difference in delaminating force between delaminating papers 102HH and 102H is provided. For providing a difference in delaminating force, a releasing layer coated on a substrate film of delaminating paper may be changed. Delaminating paper of grades called, by those skilled in the art, strong delaminating type, intermediate delaminating type, weak delaminating type, re- delaminating type and the like are commercially available and may appropriately be selected among them.

[0065]

(Measuring Method of Breaking Strain of Volume Hologram Layer)

The breaking strains of the volume hologram layer at 25°C at 120°C is obtained by an automatic record of a stress-strain curve (S-S curve) using the following measuring apparatus and measuring conditions, and the breaking strain of the volume hologram layer is read from this curve.

For a measuring sample (test piece), a material of which measurement is intended is applied on a substrate, if necessary dried or treated, then, a test piece in the form of film, delaminated from the substrate, having a width of 5 mm to 10 mm and a length of 20 mm to 50 mm is given. The thickness of the test piece is preferably in a range of 20 μ m to 100 μ m from the standpoint of easy handling. When a delaminating treatment is conducted on the surface of the substrate, it is easy to delaminate the test piece in the form of film.

(1) Breaking strain at 25°C

* Measuring apparatus: INSTRON universal tester (manufactured by MERLIN, trade name)

* Tension speed: 2 mm/min

(3) Breaking strain at 120°C

* Measuring apparatus: solid viscoelasticity analyzer RSA-2 (manufactured by Rheometric Scientific)

* Measuring tool (attachment): for film orientation

* Measuring Mode: Strain Rate Sweep

* Tension speed: 3.5×10^{-4} /sec

[0066]

(Measuring Method of Breaking Strain of Heat Sensitive Adhesive Layer)

For a measuring method of the breaking strain of the heat sensitive adhesive layer of the present invention, a heat sensitive adhesive agent is applied on PET, which had been subjected to a surface delaminating treatment, so that the thickness after drying is 20 μm , and the breaking strain was measured by the following measuring method according to JIS-K-7127.

(Measuring method)

An INSTRON universal tester manufactured by MERLIN is used as a measuring apparatus. A measuring sample having a width of 25 mm and a length of 50 mm was measured under atmosphere of 25°C and with a tension speed of 2 mm/min.

[0067]

(Evaluation of Heat Transferring Property of Transfer Foil)

A surface delaminating -treated PET film was delaminated from a volume hologram transfer foil and thermally transferred

to a card made of polyvinyl chloride under conditions of a temperature of 140°C, a pressure of 3 MPa and a period of 0.8 seconds, and transferring properties to a transferred material such as a foil cutting property, generation of burr, and the like were observed.

[0068]

[EXAMPLES]

(Example 1)

[Preparation of materials]

A first film having a hologram forming layer (PET film/volume type hologram forming material/surface delaminating treated PET film), a third film having a delaminating layer (delaminating layer/PET film) and a second film having a heat sensitive adhesive layer to which fine particles had been added (heat sensitive adhesive layer/surface delaminating PET film) were separately prepared in respective independent processes.

The first film was produced by coating the following photosensitive material composition on a PET film (Lumirror T60 (50 μm); manufactured by Toray Industries, Inc.) so that the dry thickness was 10 μm , and laminating a surface delaminating treated PET film (manufactured by TOHCELLO. CO, SP-PET (38 μm)).

Photosensitive material composition

* Polymethylmethacrylate-based resin (molecular weight 200000)

500 parts by weight

* 3,9-diethyl-3'-carboxymethyl-2,2'-thiacarboxyanine iodine salt

5 parts by weight

- * Diphenyl iodonium hexafluoro antimonate
60 parts by weight
- * 2,2'-bis[4-(acryloxydiethoxy)phenyl]propane
800 parts by weight
- * Pentaerythritol polyglycidyl ether
800 parts by weight

The third film was produced by coating the following delaminating layer composition on a PET film (Lumilar T60 (50 μm); manufactured by Toray Industries, Inc.) so that the dry thickness was 2 μm .

Delaminating layer composition

- * Polymethyl methacrylate resin (Mw=35000)
97 parts by weight
- * Polyethylene wax (Mw=10000)
3 parts by weight
- * Polyester (Mw=1500)
0.3 part by weight
- * Methyl ethyl ketone
200 parts by weight
- * Toluene
200 parts by weight

The second film was produced by coating the following heat sensitive adhesive layer composition on a surface delaminating treated type PET film (SP-PET (50 μm); manufactured by TOHCELLO. CO) so that the thickness after drying was 3 μm .

Heat sensitive adhesive layer composition

- * Heat sensitive adhesive (A-928; manufactured by Dainippon Ink

and Chemicals, Incorporated)

100 parts by weight

* Silica fine particle (average particle size: 50 nm)

20 parts by weight

* Toluene

600 parts by weight

* Methyl ethyl ketone

100 parts by weight

[Lamination of hologram recording delaminating surface protective layer]

First, a surface delaminating treated PET film was delaminated from one surface of the first film on which Lippman hologram had been recorded by using laser ray having a wavelength of 514 nm and heated at 100°C for 10 minutes, and on the delaminated surface, the surface of the surface protective layer of the third film was laminated at 80°C. By this, a laminating body composed of PET film/delaminating layer/volume hologram layer/PET film was obtained.

[Lamination of heat sensitive adhesive layer]

Next, the hologram layer was subjected to a fixing treatment by irradiation at 2500 mJ/cm² by using a high pressure mercury lamp, then, a PET film which contacts to the volume hologram was delaminated, and on the delaminated surface, the surface of the heat sensitive adhesive of the second film was laminated at 130°. By this, a laminating body of a volume hologram transfer foil of the present invention was obtained composed of PET film/ delaminating surface protective layer/

volume hologram layer/ heat sensitive adhesive containing fine particle/surface delaminating treated PET film.

The hologram layer in Example 1 had a breaking strain of 6% at 25°C and 13% at 120°C. The adhesive of the heat sensitive adhesive layer had a breaking strain of 6.4% at 25°C. Regarding a transferring property, a foil cutting property was excellent. A transfer foil showing a bright hologram image and providing very easy observation was obtained.

[0069]

(Comparative Example 1)

[Preparation of materials]

For films other than the second film (heat sensitive adhesive layer), the same materials as used in Example 1 are used.

The second film was produced by coating the following heat sensitive adhesive layer composition on a surface delaminating treated PET film (SP-PET (50 μm); manufactured by TOHCELLO. CO) so that the dry thickness was 3 μm .

Heat sensitive adhesive layer composition

* Heat sensitive adhesive (A-928; manufactured by Dainippon Ink and Chemicals, Incorporated)

100 parts by weight

* Toluene

600 parts by weight

[Production of hologram transfer foil]

A volume hologram transfer foil composed of PET film/ delaminating surface protective layer/ volume hologram/ heat

sensitive adhesive not containing fine particle/surface delaminating treated PET film was obtained. In the volume hologram transfer foil in Comparative Example 1, the adhesive of the heat sensitive adhesive layer had a breaking strain at 25°C of 20% or more. Regarding a transferring property, a foil cutting property was poor, burr was generated, and excellent transfer to a transferred body was impossible because of elongation of the heat sensitive adhesive.

[0070]

(Example 2)

A volume hologram transfer foil was obtained in the same manner as in Example 1 except that Luminova G-300 F having an average particle size of 10 μm (manufactured by NEMOTO & CO., LTD., trade name of fluorescent pigment) was used as a fluorescent fine particle instead of the silica fine particle. In the volume hologram transfer foil, the adhesive of the heat sensitive adhesive layer had a breaking strain at 25°C of 13.5%. Regarding a transferring property, a foil cutting property was excellent. A transfer foil showing a bright hologram image and providing very easy observation was obtained.

[0071]

(Example 3)

A volume hologram transfer foil was obtained in the same manner as in Example 1 except that 50 parts by weight of bead pigment (manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd., urethane elastic bead with the most-popular-particle size thereof of 23 μm) was used as resin bead pigment instead of 20 parts by weight of the silica fine particle. In the volume hologram transfer foil, the adhesive of the heat sensitive